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HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

TEST PLAN

AROMATIC EXTRACTS CATEGORY

Submitted to the US EPA

By

The Petroleum HPV Testing Group

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PLAIN LANGUAGE SUMMARY

This plan addresses the potential mammalian and environmental hazard of exposure to aromatic extracts. This material is a complex mixture of predominately aromatic hydrocarbons covering the carbon number range of C15 to C54. Aromatic extracts are produced as byproducts when lubricating oil base stocks and waxes are extracted to remove aromatic hydrocarbons. These highly viscous to mobile liquids are used in heavy fuels, as precursors in the synthesis of carbon black, petroleum pitches and resins, and in the manufacture of rubber and plastics. Aromatic extracts are classified as either "distillate" aromatic extracts (DAE), or "residual" aromatic extracts (RAE), depending on whether they were produced from the extraction of distillate lubricating oil base stocks or residual lubricating oil base stocks.

There is a large body of toxicity data relating to aromatic extract and other compositionally related heavy petroleum streams that dates back over 50 years. Untreated aromatic extracts produce skin cancer in the mouse, and can possibly cause cancer of the respiratory tract upon inhalation of aerosols of the material. Numerous studies have shown that the mutation and cancer causing potential of aromatic extracts is directly related to the presence of 3-7 ring polycyclic aromatic compounds contained in the extract. The testing group also believes that this same correlation exists for other mammalian toxicity endpoints.

DAE has a low order of acute oral and dermal toxicity. Although no acute toxicity studies were reported for RAE, RAE toxicity would be expected to be less that DAE due to the higher molecular weights and higher viscosities of the components. DAE caused mutations in the modified Ames test and in the mouse lymphoma assay. Evaluation of genetic material in rats exposed repeatedly to either DAE and RAE did not show any adverse effects. A number of repeated dose toxicity studies have been conducted on different samples of aromatic extract. Repeated oral or dermal dosing of DAE produced toxic effects in the liver, thymus and blood. Repeated skin applications of RAE also produced similar albeit less significant toxic effects depending on dose. Microscopic examination of male and female reproductive organs in these studies did not reveal any toxic effects due to treatment. DAE caused toxicity to the developing fetus when applied to the skin of pregnant rats during days 0-19 of gestation. However, these effects occurred only in the presence of toxic effects in the mothers. In a similar study, RAE did not produce any adverse developmental effects.

The environmental fate and hazard of aromatic extracts is determined by the individual hydrocarbons present within the mixture. Aromatic extracts are highly viscous liquids having component hydrocarbons that have melting points at or above ambient temperatures. These substances will tend to clump together rather than disperse if released to the environment. They also have very low vapor pressures, although individual hydrocarbon compounds at the lower molecular weight range (i.e., C15 compounds) may evaporate during weathering. Aromatic extracts are not expected to partition to water, because their water solubility is also very low. Modeled partition coefficients of the low molecular weight hydrocarbons (e.g., C15 compounds) typically exceed 5, with higher molecular weight hydrocarbons having partition coefficients >20. Modeling the environmental distribution shows that components generally partition to soil. Individual components that evaporate would be expected to undergo rapid indirect

photodegradation. Once released to the environment, aromatic extracts are not likely to undergo rapid biodegradation.

DAE or RAE have not demonstrated acute toxicity to freshwater fish, invertebrates or algae due to water solubility limitations. Toxicological endpoints for acute effects were >1000 mg/L when applied as water accommodated fractions (WAF). Reproduction and survival was unaffected in adult aquatic invertebrates (*Daphnia magna*) exposed for 21 days to >1000 mg/l WAF fractions of DAE and RAE. Offspring produced during the test also appeared healthy with no adverse effects noted.

The testing group feels that the existing physicochemical, mammalian toxicology and environmental information adequately characterize the potential health and environmental effects of aromatic extracts.

DESCRIPTION OF THE AROMATIC EXTRACTS CATEGORY

General Information

As used in this Test Plan, "aromatic extract" refers to extracts of vacuum distillates or residuum that have not been subjected to further processing such as hydrogenation, desulfurization, clay or acid treatment, additional distillation or solvent extraction. Other terms used for aromatic extracts are aromatic process oil, bright stock extract, distillate aromatic extract, process oil, solvent extract, rubber extender oil, and residual aromatic extract.

Aromatic extracts are highly viscous to mobile liquids, which may be dark amber to black in color. Boiling points of components are above 650^{o}F at atmospheric pressure.

Aromatic extracts are used in applications where their solvency is valued, but also as components of heavy fuel blends (e.g., industrial fuel oil, bunker fuel) and as precursors for synthesis of other hydrocarbon products (e.g., carbon black, petroleum resins, and petroleum pitch). Within a refinery, aromatic extracts can also be converted to other refinery products by processes such as cracking and coking to light hydrocarbon fuels or coke. In rubber and plastic manufacture, aromatic extracts are used as extenders, softeners and diluents that remain in the final product contributing to both ease of processing and improved product performance. Very large quantities are employed in tire manufacture, and lesser amounts for specialty applications such as asphalt blends and seal coatings. Highly aromatic streams, including the aromatic extracts, are also used as feedstock for making carbon black, petroleum resins, and petroleum pitch.

Production of Aromatic Extracts

Aromatic extracts are produced as byproducts in the refining of lubricating oil basestocks and waxes. The residue (residuum) of atmospheric distillation of crude oil is distilled under vacuum to produce distillate and residual lubricating oil basestocks. These lubricating oil basestocks have been described in the Lubricating Oil Basestocks Category. The untreated (raw or straight-run) lubricating oil basestocks contain undesirable components that negatively impact lubricant performances, i.e., color, odor, stability and/or viscosity that must be removed. These components include aromatic compounds containing sulfur, nitrogen, and oxygen as heteroatoms and polycyclic aromatic compounds.

The aromatic extracts can be grouped into two subcategories, according to the class of lubricating basestock refinery stream from which they are derived, namely, distillate aromatic extracts (DAE) and residuum aromatic extracts (RAE).

Distillate Aromatic Extracts (DAE)

Straight run distillates (lubricating oil basestocks) are extracted with a solvent such as furfural, phenol, or N-methyl-2-pyrrolidone (NMP) to selectively remove the undesirable aromatic compounds, (especially 3-7 fused ring PAC). Other solvents such as dimethyl sulfoxide (DMSO) can also be used. The solvent is then stripped from the resulting extract, and the remaining aromatic concentrate (aromatic extract) is either sold as is or further treated (treated DAE) for specialty applications. As in the case of the distillates, the viscosity of the aromatic extract

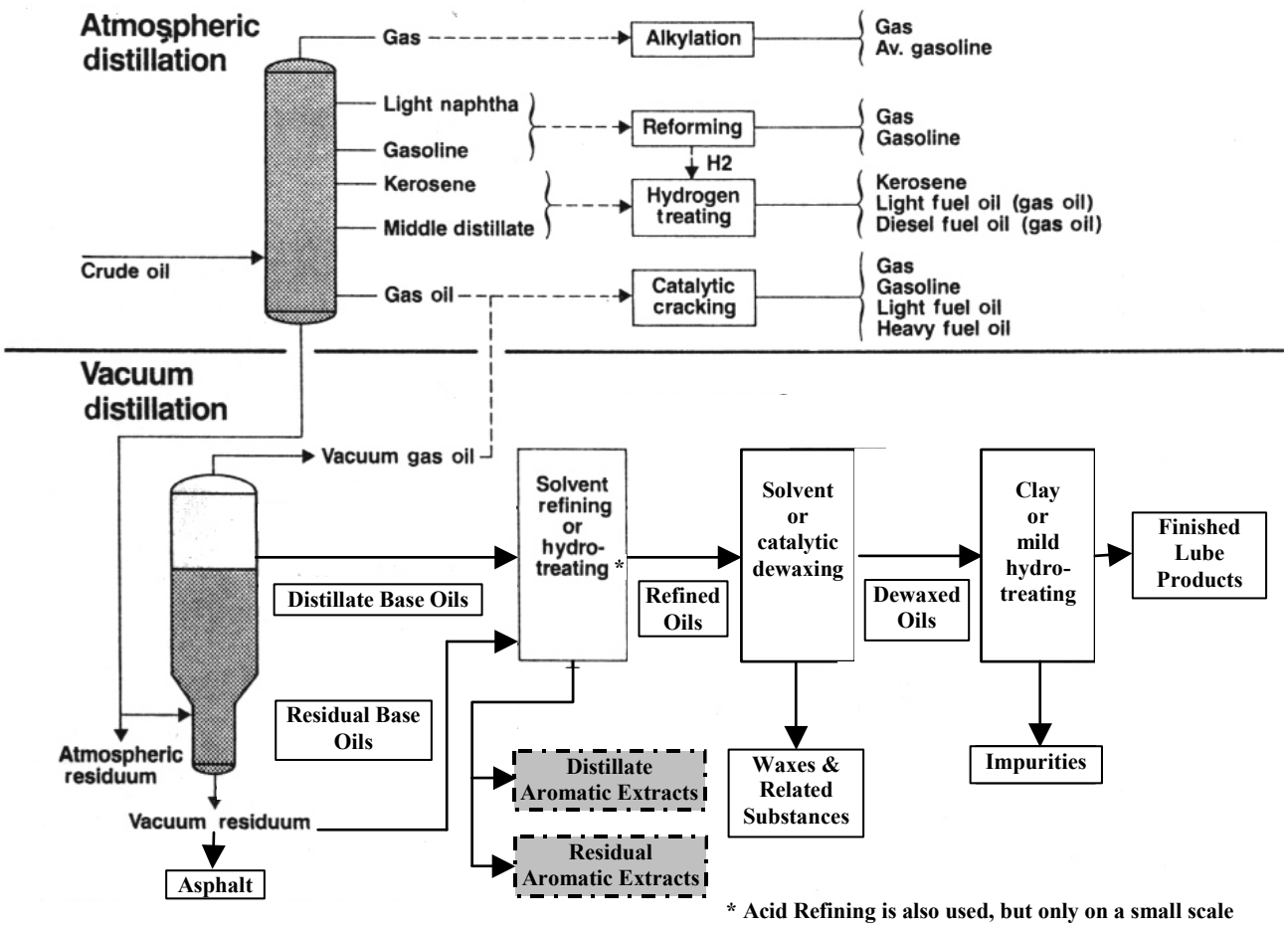
increases with increasing boiling range (Briggs and Mackerer, 1996; Roy et al., 1996). Distillate aromatic extracts may also be called aromatic process oil, distillate aromatic extract, process oil, solvent extract, and rubber extender oil.

Residual Aromatic Extracts (RAE)

The residuum from vacuum distillation is extracted with liquid propane to remove particulates, resins, and asphaltenes. In this process, the resins, asphaltenes and particulates precipitate out and the propane/oil stream is then stripped of the propane. The very viscous stream that results is referred to as deasphalted oil (DAO). The DAO undergoes the same extraction process used for the vacuum distillate streams. Residual aromatic extracts may also be called bright stocks or bright stock extracts. As with DAE, RAE viscosity increases with increasing boiling range (Briggs and Mackerer, 1996; Roy et al., 1996).

A refining diagram showing both lubricating oil basestocks and aromatic extracts production is presented in Figure1.

Fig. 1. Simplified processing plan for a petroleum refinery



Physical and Chemical Properties of Aromatic Extracts

The range of physical and chemical properties is shown in Table 1. Composition information on representative samples of three DAE and three RAE are shown in Table 2. Aromatic extracts are derived from purification of distillate and residual refinery streams boiling between 650 and 1000+F, respectively, via solvent refining (extraction) during the manufacture of lubricating oil basestocks. Aromatic compounds including those containing sulfur, nitrogen, and oxygen removed from these processes are the major constituents of the aromatic extracts. The number of different chemical components and their molecular weights increase in the extracts as the boiling point ranges increase.

As can be seen in Table 2, Untreated DAE are generally composed of approximately 60-78% aromatics with one-two ring aromatic hydrocarbons (PAH) representing 28-35% and 3-5 ring PAHs representing 17-23% of the aromatic fraction. The remaining balance is naphthenic and

isoparaffinic hydrocarbons. Untreated RAE are generally composed of approximately 81-92% aromatics with one-two ring PAHs representing 37-40% and 3-5 ring PAHs representing 20-23% of the aromatic fraction. Aromatic concentrations in either DAE or RAE are largely dependant on the source and type of crude from which the extract is processed (Feuston et al., 1994).

Superficially, the levels of the different types and classes of aromatic, naphthenic and aliphatic compounds in DAE and RAE do not appear to be substantially different when one considers only number of aromatic rings and naphthenic/aliphatic content. However, in the RAE, the molecular weights of the components are generally much higher, the naphthenes and aromatics have more and larger side chains and there are substantial amounts of polycyclic naphthenes. As the paraffinic and naphthenic side-chains increase in size and number, the molecules become more paraffinic in nature, are less soluble in aromatic specific solvents and the number of extractable 3-7 ring PAC are also reduced. As noted in Table 2, the range of 3-7 ring PAC concentration by DMSO extraction is significantly lower, i.e., 0.8-8% for RAE compared to 5-73% for DAE. This is largely due to increased RAE paraffinicity.

Category Members

Distillate aromatic extracts

Extract	Hydrocarbon chain length	CAS number
1) Extract, distillate, light paraffinic	C15-C30	64742-05-8
2) Extract, distillate, light naphthenic	C15-C30	64742-03-6
3) Extract, distillate, heavy paraffinic	C20-C50	64742-04-7
4) Extract, distillate, heavy napthenic	C20-C50	64742-11-6
Residuum aromatic extracts		
5) Extract, residuum	C25+	64742-10-5

CATEGORY RATIONALE

The Testing Group's rationale for grouping these materials into a single category is as follows:

1. Category members of the DAE and RAE are refined via a similar refinery process.
2. Toxicity of both DAE and RAE is proportional to the concentration of DMSO extractable 3-7-ring PAC (Feuston et al., 1994; Roy et al., 1988).
3. DMSO extractable 3-7-ring PAC are identical in both DAE and RAE, but levels are higher in DAE.

4. Since toxicity is related to DMSO extractable PAC content, the data for any one of the four DAE streams is representative of the entire category of distillate aromatic extracts.

EVALUATION OF EXISTING HEALTH EFFECTS DATA AND PROPOSED TESTING

Acute Toxicity

Distillate Aromatic Extracts

Distillate aromatic extracts have low acute systemic toxicity. Oral LD50s for both light and heavy DAE were greater than 5000 mg/kg (API, 1986a; FDRL, 1974a). Dermal LD50s for the same two samples were greater than 2000 mg/kg (API, 1986a; FDRL, 1974b) but produced skin irritation and transient eye irritation (API, 1986a; FDRL, 1974c,d). DAE did not produce sensitization in a Buehler guinea pig skin sensitization assay (API, 1986a).

Residual Aromatic Extracts

No acute toxicity studies have been reported for RAE. However, due to the higher molecular weights and higher viscosities of the components, RAE toxicity would be expected to be less than DAE.

Summary: No additional acute toxicity testing is planned. There is adequate data to characterize the acute toxicity end points of both distillate and residual aromatic extracts.

Repeat-Dose Toxicity

Distillate Aromatic Extracts

In a 28-day study, rabbits received dermal applications of 0, 250, 500 and 1000 mg/kg of neat DAE to shaved backs once/day, 3 times/week, for a total of thirteen DAE applications. After each application, the site was occluded for 6 hours and then wiped free of DAE. Body weights and food consumption were measured and the animals were observed for clinical signs of toxicity. Hematology and clinical chemistries were performed; multiple organs were weighed, and gross and microscopic pathological examinations were performed. The only possible treatment-related effects noted were increased relative liver weight among females at all dose levels of DAE. DAE produced skin irritation in both sexes, with slight to severe proliferative changes observed microscopically in skin of the high dose group (API, 1986b).

In a second study, distillate aromatic extract was administered dermally without occlusion to the shorn backs of male and female rats, 5 days/week for thirteen weeks at doses of 0, 30, 125, 500, and 1250 mg/kg. In addition, two extra groups of 10 male rats received oral doses of 125 and 500 mg/kg/day for 13 weeks (Mobil, 1990a; Feuston et al., 1996; Feuston et al., 1994). Evidence of toxicity included mortality, decreased body weight, aberrant serum chemistry and hematology parameters, altered organ weight, and histopathological changes in several organs. Histopathological evaluations of the male and female reproductive organs were conducted on animals at the highest non-fatal dose of DAE (125mg/kg/day dermally and 500 mg/kg/day orally) and gonads, epididymides, prostates, and seminal vesicles were examined microscopically. These organs were characterized as “small” but without any histopathological effect. Epididymal spermatozoa

morphology and count and testicular spermatid counts were examined and found to be unaffected by treatment.

Residual Aromatic Extracts
Four samples of RAE were tested for subchronic dermal toxicity in the rat, at 500 and 2000 mg/kg/day for 13 weeks according to the same procedure used for DAE described above (Mobil, 1990b). At 500 and 2000 mg/kg, there were no changes in body weight, no clinical signs of toxicity, and no observations of skin irritation. In both sexes there were several small changes in serum chemistry and hematology parameters. Relative spleen and liver weights were increased at 2000 mg/kg. There were no treatment related pathological effects seen after gross or microscopic examination of organs and tissues, including those of the male and female reproductive organs. Epididymal spermatozoa morphology and count and testicular spermatid counts were examined and found to be unaffected by treatment. These RAE were observed to be significantly less toxic that DAE, probably due to the relatively lower concentrations of 3-7 ring PACs and higher viscosity that substantially reduces absorption (Potter et al., 1999).

Summary: No additional repeat-dose toxicity testing is planned. There is sufficient data to characterize the subchronic toxicity of both distillate and residual aromatic extracts.

Genotoxicity
***In Vitro* (Mutagenicity)**
Distillate Aromatic Extracts
Gene mutation assays performed in *Salmonella typhimurium* strain TA 98 with metabolic activation in an Ames test, modified to enhance contact between the bacterial cells and the highly insoluble oil components, have shown that DAE are mutagenic and that the mutagenic potency is correlated with the concentration of 3-7 ring PAC-enriched fraction obtained by extraction with DMSO, and with dermal carcinogenic activity in the mouse (Roy et al., 1988; Blackburn et al., 1984 a, b).

The mouse lymphoma forward mutation assay has been performed for DAE using cell line L5178Y. DAE was found to be mutagenic with and without activation, and a dose response was observed with activation. The DAE was dissolved in ethanol, and was visibly insoluble in the media at higher doses (API, 1986c).

Residual Aromatic Extracts
Some RAE were mutagenic in the modified Ames test. The biological activity is related to the presence and level of DMSO extractable 3-7 ring PAC (Blackburn et al., 1996).

Summary: No additional *in vitro* mutagenicity testing is planned. There is sufficient data to characterize the *in vitro* mutagenicity of both distillate and residual aromatic extracts.

***In Vivo* (Chromosomal Aberrations)**

Distillate Aromatic Extracts

In vivo micronucleus evaluations were performed on bone marrow harvested at termination of the thirteen-week oral and dermal assay of DAE described in the repeat-dose toxicity section. No treatment-related increase in micronuclei was observed (Mobil, 1987).

Residual Aromatic Extracts

In vivo micronucleus evaluations were performed on bone marrow harvested at termination of the subchronic dermal assays of RAE described in the repeat-dose toxicity section. No treatment - related increase in micronuclei was observed (Mobil, 1988).

Summary: No additional *in vivo* genotoxicity testing is planned. There is sufficient data to determine the *in vivo* genotoxicity of both distillate and residual aromatic extracts.

Carcinogenicity

Carcinogenicity testing is beyond the scope of HPV, but it should be noted for information purposes that many studies have been performed to evaluate the dermal carcinogenicity of aromatic extracts in the mouse. Numerous studies have shown that the mutagenic and carcinogenic potential of aromatic extracts and other compositionally related heavy petroleum streams correlates with the presence of 3-7 ring polycyclic aromatic compounds (Roy et al, 1988; Blackburn et al., 1984b; Cruzan et al., 1986; Blackburn et al., 1986). Further studies have shown these PACs can be absorbed through the skin and enter the general circulation (Roy et al., 1996; Roy et al., 1998). Untreated DAE has been shown to be a potent dermal carcinogen in a number of mouse skin painting bioassays (IARC, 1984). The dermal carcinogenicity of untreated RAE has ranged from non-carcinogenic to moderately carcinogenic (Blackburn, 1996; Reddy et al., 1997; Kane et al., 1984; Doak et al., 1985; Gradiski et al., 1983; Bingham et al., 1980; King, D.J., 1991; Shell Research Ltd., 1991).

Reproductive/Developmental Toxicity

Distillate Aromatic Extracts

In a prenatal developmental toxicity study, neat DAE was applied dermally to rats at 0, 8, 30, and 125 mg/kg/day on gestation days 0-19. The application site was not occluded and the site was not wiped after dosing. Rats wore Elizabethan collars to retard oral ingestion. End points of toxicity included body weight, food consumption, hematology, serum chemistry, liver weight, thymus weight, fetal resorption, anomalous development (skeletal and visceral) and fetal body weight (Mobil, 1990c; Feuston et al., 1996). For maternal and developmental endpoints, statistically significant effects occurred only at 125 mg DAE/kg/day. The maternal effects included decreased body weight and gain, gravid uterine weight, increased liver weight, decreased thymus weight, increased white blood cell count, and alterations in most of the serum chemistry parameters. The developmental effects included increased number of dams with resorptions, reduced litter size, decreased fetal body weight, and increased resorptions. Fetal effects occurred only at the concentration that caused significant maternal effects. Developmental toxicity was observed in the female rat from DAE but this was considered to be secondary to maternal toxicity.

No reproductive toxicity studies were identified for DAE. However, no histopathological changes were observed in the reproductive organs of male and female rats via the oral or dermal route of exposure in the 13-week subchronic studies described in the repeat-dose section above. Epididymal spermatozoa morphology and count and testicular spermatid counts were unaffected by DAE treatment (Mobil, 1990a).

Residual Aromatic Extracts
In a developmental toxicity study similar to that described for DAE in the preceding section, RAE was applied dermally to pregnant rats at doses of 500 and 2000 mg/kg RAE from days 0-19 of gestation, and 2000 mg/kg from day 0 of gestation to day 4 of lactation. No maternal or developmental toxicity was seen (Mobil, 1989).

No reproductive toxicity studies were identified for residual aromatic extracts. However, a thirteen-week dermal study was conducted on multiple samples of residual aromatic extract in male and female rats, in which no histopathological effects were found in the reproductive organs. Epididymal spermatozoa morphology and count and testicular spermatid counts were unaffected by RAE treatment (Mobil, 1990b).

Summary: No additional reproductive/developmental toxicity testing is planned. There is sufficient data to characterize the reproductive/developmental toxicity of both distillate and residual aromatic extracts.

EVALUATION OF EXISTING PHYSICOCHEMICAL AND ENVIRONMENTAL FATE DATA

General
The substances covered under this HPV testing plan are mixtures of differing compositions. Because they are mixtures, it is not possible to measure or calculate a single numerical value for most of the physicochemical properties. The range of individual hydrocarbon components in aromatic extracts defines these properties. For example, an aromatic extract does not have a defined melting point, but rather a melting point range. Therefore, melting point, boiling point, and partition coefficient will be reported as ranges of individual components reflective of the compositional analysis of aromatic extracts. An exception is vapor pressure, which is a measure of the total partial pressure exerted by the components of a mixture.

Although some data for products in this category exist, not all of these endpoints are defined and a consensus database for chemicals that represent products in this category does not exist. Therefore, calculated and measured representative data have been identified and included in the robust summaries where appropriate. The EPIWIN© computer model (U.S. EPA 2000), as discussed in the U.S. EPA document entitled "*The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program*" was used to calculate physicochemical properties of representative constituents for selected aromatic extract streams. Because of the diversity of compounds making up aromatic extracts, it was not feasible to model the physicochemical endpoints for each potential component. Instead, modeling efforts were directed

toward representative hydrocarbon compounds in aromatic extracts that are most likely to partition to various environmental media, yet still encompass the typical extremes in molecular weight.

Melting Point

To better describe the physical phase or flow characteristics of petroleum products, the pour point is routinely used instead of the melting point. The pour point is the lowest temperature at which movement of the test specimen is observed under prescribed conditions of the test (ASTM 2002). The pour point methodology also measures a "no-flow" point, defined as the temperature of the test specimen at which a wax crystal structure and/or viscosity increase such that movement of the surface of the test specimen is impeded under the conditions of the test (ASTM 2002). Because not all petroleum products contain wax in their composition, the pour point determination encompasses change in physical state (i.e., wax crystal formation) and/or viscosity. The pour point measured for distillate aromatic extracts ranged from –6 °C to +36 °C, whereas pour point for residual aromatic extracts is considered as > +20 °C (CONCAWE, 1992).

Summary: No additional testing is proposed. The pour point of various aromatic extracts has been adequately measured.

Boiling Point

As mixtures, aromatic extracts do not have a single numerical value for boiling point, but rather a boiling range that reflects the individual components. The production of aromatic extracts results in two distinct streams that have slightly differing components that affect the boiling range of those products. Aromatic extracts from the distillate fraction of the production process generally have the boiling range of 250 to 680° C, while aromatic extracts from the residuum fraction boil at >380 °C (CONCAWE, 1992).

Summary: No additional testing is proposed. The boiling range of aromatic extracts has been adequately addressed.

Vapor Pressure

For mixtures such as petroleum products, the vapor pressure of the mixture is the sum of the partial pressures of the individual components (Dalton's Law of Partial Pressures). Aromatic extracts are expected to have low vapor pressure due to their high viscosity, boiling range and molecular weights of the constituent hydrocarbons (C_{15} – C_{50} carbon atoms). Vapor pressure for distillate and residual aromatic extracts have been measured to be <0.1 hPa (CONCAWE, 1992).

Summary: No additional testing is proposed. The vapor pressure of distillate and residual aromatic extracts has been adequately measured.

Partition Coefficient

Aromatic extracts consist of mixtures of hydrocarbon groups having carbon numbers in the range C_{15} to C_{50}. The percent distribution of the hydrocarbon groups (i.e., isoparaffins, naphthenes, and aromatics) and the carbon chain lengths contribute to determining the partitioning characteristics of the mixture. Generally, hydrocarbon chains with fewer carbon atoms tend to have lower partition coefficients than those with higher carbon numbers (CONCAWE, 2001). However, due to their

complex composition and low water solubility, measurements of the log K_{ow} of these hydrocarbon mixtures typically cannot be made. For example, one study of the partitioning behavior of a DAE found that 85% of the components in the DAE had partition coefficients greater than the applicable range (log K_{ow} of 0 to 6) for the method (Shell Research Ltd., 1984a, 1994b). Modeling efforts also support this study. Partition coefficients of selected C_{15} and C_{50} chain-length hydrocarbon structures representing paraffinic, naphthenic, and aromatic constituents in aromatic extracts were modeled using EPIWIN©, KOWWIN V1.66 (U.S. EPA, 2000). Results showed log K_{ow} values ranged from approximately 5 and to greater than 7 for the C_{15} components, while values for C_{50} compounds were greater than 20.

Summary: No additional modeling is proposed. The partition coefficients of distillate and residual aromatic extracts have been adequately measured.

Water Solubility

For individual components in aromatic extracts, water solubility values vary by orders of magnitude. Molecular weight and chemical structure influence the ultimate degree of solubility. Solubility typically decreases with increasing molecular weight, while aromatic hydrocarbons show greater water solubility than saturated hydrocarbons for compounds of equal carbon numbers. Water solubility estimates were obtained for representative paraffinic, naphthenic, and aromatic hydrocarbon structures in aromatic extracts using WSKOW V1.40 (EPIWIN V3.10, EPA, 2000). Estimates for the low molecular weight C_{15} compounds ranged from <0.001 for various saturated hydrocarbons to 0.63 mg/l for a C_{15} two-ring aromatic structure. Solubility values for all C_{50} hydrocarbon structures were extremely low, with estimates on the order of 10^{-18} mg/l or lower. CONCAWE (1992) reported water solubility values of "negligible" for residual aromatic extracts and 1.4 and 5.8 mg/l for distillate extracts. However, those data were not referenced in this document and could not be verified. Attempts to measure soluble fractions of distillate and residual aromatic extracts in water accommodated fractions by GC/MS during aquatic toxicity testing have failed to detect levels greater than those found in control water (BP Oil Europe 1995 a, b).

Since aromatic extracts are viscous, semi-solid to solid materials at ambient temperatures, water solubility is expected to be negligible for these materials.

Summary: No additional modeling is proposed. Water solubility values have been measured for distillate and residual aromatic extracts.

Photodegradation

The direct aqueous photolysis of an organic molecule occurs when it absorbs sufficient light energy to result in a structural transformation. Only light energy at wavelengths between 290 and 750 nm can result in photochemical transformations in the environment, although absorption is not always sufficient for a chemical to undergo photochemical degradation. Saturated and one-ring aromatic hydrocarbons do not show absorbance in the 290-to 800 nm range and would not be expected to be directly photo degraded. Polyaromatic hydrocarbons, on the other hand, have shown absorbance of this range of light energy and could potentially undergo photolysis reactions. The degree and rate at which these compounds photo degrade will depend upon whether conditions allow penetration of

light with sufficient energy to effect a change. For example, polyaromatic compounds bound to sediments may persist due to lack of adequate light penetration.

Components in aromatic extracts that do not directly photo degrade (e.g., paraffins, naphthenes, and one-ring aromatic compounds) may be subject to indirect photodegradation. Indirect photodegradation is the reaction with photosensitized oxygen in the atmosphere in the form of hydroxyl radicals (OH). The potential to undergo indirect photodegradation can be estimated using the atmospheric oxidation potential (AOP) model subroutine (AOPWIN V1.90) in EPIWIN© (EPA, 2000), which calculates a chemical half-life and an overall OH^- reaction rate constant based on a 12-hour day and a given OH^- concentration. Atmospheric oxidation rates and half-lives were calculated for the lowest molecular weight constituents of various components of aromatic extracts. (e.g., C_{15} hydrocarbon structures), since these would have the most potential to volatilize to the atmosphere. AOP half-life estimates for these compounds ranged from 0.1 to 0.7 days and show a lack of persistence in the atmosphere.

Since aromatic extracts are highly viscous materials with low volatility, the importance of direct and indirect photodegradation as an overall fate pathway may be slight. However, if conditions result in dispersion or volatilization where sunlight and photosensitized oxygen compounds may interact with components of aromatic extracts, it is unlikely that those compounds will persist in the environment.

Summary: No additional modeling is proposed. Atmospheric oxidation potential of representative C_{15} components in aromatic extracts have been modeled.

Stability in Water

Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Harris, 1982). Because aromatic extracts do not contain significant levels of these functional groups, components in the aromatic extracts category are not subject to hydrolysis.

Summary: Computer modeling will not be conducted for components in the aromatic extracts category because they do not undergo hydrolysis.

Chemical Transport and Distribution in the Environment (Fugacity Modeling)

Fugacity-based multimedia modeling can provide basic information on the relative distribution of chemicals between selected environmental compartments (e.g., air, water, soil, sediment, suspended sediment and biota). The US EPA has agreed that computer-modeling techniques are an appropriate approach to estimating chemical partitioning (fugacity is a calculated endpoint and is not measured). A widely used fugacity model is the EQC (Equilibrium Criterion) model (Trent University, 1999). The EQC model is a Level 1 (i.e., steady state, equilibrium, closed system and no degradation) model that utilizes the input of basic chemical properties including molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. EPA cites the use of this model in its document "Determining the Adequacy of Existing Data" that was prepared as guidance for the HPV chemicals program (U.S. EPA, 1999).

To gain an understanding of the potential transport and distribution of aromatic extracts, the EQC model was used to characterize the environmental distribution of various C_{15} and C_{50} compounds representing different structures in aromatic extracts (e.g., isoparaffins, naphthenes, and aromatics). Modeling results show that aromatic extracts released to the environment would bind to soil/sediment with only negligible amounts dissolving in water. Some of the lower molecular weight paraffins, isoparaffins, naphthenes and 1-ring aromatic component hydrocarbons may partition to the air over time and weathering of the materials. However, these would be expected to undergo reaction with atmospheric hydroxyl radicals and not persist.

Summary: No further modeling is proposed. Fugacity modeling has been done to provide an estimate of the percent distribution in environmental media of various C_{15} and C_{50} hydrocarbons found in aromatic extracts.

Biodegradation

Aromatic extracts have not demonstrated a capacity to readily biodegrade in laboratory tests (Shell Research Ltd, 1994a). In two 28-day ready biodegradability studies on a distillate aromatic extract, no biodegradation was measured when using the modified Sturm and closed bottle test protocols. Similar results would be expected for residual aromatic extracts based upon the higher molecular weight components in those materials. However, since component hydrocarbons are considered inherently biodegradable (CONCAWE, 1992), some time would be expected for adapted microbial populations to develop the capability to utilize those components.

Summary: No further testing is proposed. Adequate information exists on the ready biodegradability potential of the DAE. RAE would be expected to behave similarly to the DAE.

EVALUATION OF EXISTING ECOTOXICITY DATA

Multiple acute toxicity studies with fish, invertebrates, and algae have been conducted to assess the ecotoxicity of distillate and residual aromatic extracts (BP Oil Europe 1994 a, b, c, d, e; BP Oil Europe, 1995 a, b). For fish and invertebrates, no adverse effects on survival or behavioral characteristics were found when tested up to the maximum test concentration of 1000 mg/L as water accommodated fraction (WAF). Similarly, algae were exposed to 1000 mg/L WAF preparation of RAE. No adverse effects on growth or growth rate in the algal populations were evident during the exposure. An algal test was not available for DAE, but based on the limited solubility of these materials, no toxicity would be expected.

Aromatic extracts were tested for chronic toxicity to aquatic invertebrates (*Daphnia magna*). In 21-day exposures to DAE and RAE WAF preparations, neither survival nor reproduction was impaired in the adult generation. Offspring produced during the test also appeared healthy with no adverse effects noted. For chronic exposures of DAE and RAE to aquatic invertebrates, the no-observed-effect level was considered 1000 mg/L WAF (BP Oil Europe, 1995 a, b).

Due to the variable composition of substances in this category, the two chronic toxicity studies cited may not conclusively represent chronic aquatic toxicity for all substances in this category.

However, due to the high viscosity of these materials, which are semi-solid to solid at ambient temperatures, the potential for components such as PAHs to contribute to chronic effects in aquatic organisms would be expected to be extremely limited. This is due not only to the physical state of the materials but also to the high octanol/water partition coefficients of these components, which limits the partitioning into the aqueous phase. For these reasons, it is unlikely that water accommodated fractions of aromatic extracts prepared at the chronic exposure limit concentration of 1 mg/L would elicit effects of discernible significance in standard chronic toxicity assays. This is supported by the lack of chronic toxicity at 1000 mg/L found in the studies described in the robust summaries (BP Oil Europe, 1995). Therefore, although it is not possible to accurately predict the extent of chronic aquatic effects of the water-equilibrated components for all aromatic extracts due to the variable composition, evaluation of chronic toxicity for both distillate and residual aromatic extracts indicates that no effects were discerned in aquatic organisms exposed to the water soluble components of those extracts.

Summary: No further testing is proposed. Adequate data exists on the acute aquatic toxicity of distillate and residual aromatic extracts.

Table 3. Matrix of Available Data and Proposed Testing

Test	Distillate Aromatic Extract	Residual Aromatic Extract
Melting Point	Adequate	Adequate
Boiling Point	Adequate	Adequate
Vapor Pressure	Adequate	Adequate
Partition Coefficient	Adequate	Adequate
Water Solubility	Adequate	Adequate
Photodegradation	Adequate	Adequate
Stability in Water	Adequate	Adequate
Transport and Distribution	Adequate	Adequate
Biodegradation	Adequate	Read Across[1]
Acute Toxicity to Fish	Adequate	Adequate
Acute Toxicity to Aquatic Invertebrates	Adequate	Adequate
Toxicity to Algae	Read Across [2]	Adequate
Acute Toxicity	Adequate	Read Across [1]
Repeated Dose	Adequate	Adequate
Genotoxicity, in vitro	Adequate	Adequate
Genotoxicity, in vivo	Adequate	Adequate
Repro/ Developmental	Adequate	Adequate

[1] Read Across from existing information on DAE
[2] Read Across from existing information on RAE
Adequate. Indicates adequate existing data

No additional testing is proposed for mammalian or environmental endpoints.

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Table 1

Ranges of Physical and Chemical Properties for Distillate and Residual Aromatic Extracts[1]

Property	Unit	Method	Distillate (DAE)	Residual (RAE)
Boiling Range	C	ASTM D 2887	250-680	>380
Pour Point	C	ASTM D 97	-6 to +36	> +20
Vapour Pressure, 20° C	hPa	OECD 104	<0.1	<0.1
Water solubility, 20° C	mg/l	OECD 105	1.4 – 5.8	sparingly
Flash point closed cup	C	ASTM D 93	150-270	>250
Autoignition temperature	C	DIN 51794	250-410	>380
Density, 15 ° C	kg/dm	ASTM D 1298	0.95-1.03	0.96-1.02
Viscosity, kinematic 40° C[2]	mm2/s	ASTM D 445	5-18 000	>4000
Viscosity, kinematic 100° C	mm2/s	ASTM D 445	3-60	60-330
Average Molecular Mass	–	ASTM D 2887	300-580	>400
Carbon number range	–	ASTM D 2887	C15-C54	>C25
Aromatic Content	%m	ASTM D 2007	65-85	60-80
DMSO extract[3]	%m	IP 346	10-30	not applicable

[1] Table from CONCAWE, 1992.
[2] Viscosity measurements at 40° C are subject to error
[3] By method IP 346 (IP, 1980). IP346 is not routinely applied to RAE

Table 2

Compositional Analysis of Representative Aromatic Extracts[1]

Samples	AH (% total sample)[2]					Nitrogen (ppm)		Sulfur[3]	N-PAC[3]	S-PAC[3]	Aromatics[3]	3-7 ring PAC[4]
	1R	2R	3R	4R	5R	total	basic	total %	total %	total %	total %	total %
	Distillate Aromatic Extracts (CAS No. 64742-04-7)[5]											5-73%[6]
1)[7]	21.3	15.9	9.5	7.7	5.8	2100	623	3.14	2.25	12.8	77.7	20.3
2)	14.7	13.8	9.1	6.6	6.9	2500	753	0.94	2.68	4.7	63.4	14.5
3)	20.5	14.6	7.2	6	4.2	2000	640	0.98	2.15	4.1	60.9	~15
	Residual Aromatic Extracts (furfural) (CAS No. 64742-10-5)[8]											0.8-~8.0[6,9]
4)	21.3	15.9	9.1	4.2	6.7	1100	774	1.71	1.18	6.1	81.1	NA
5)	23	15.8	9.2	4.5	8.2	2600	856	1.83	2.79	6.2	84.9	NA
6)	22.4	17.3	10.6	4.9	7.9	1500	496	3.83	1.60	13.6	91.7	NA

NA = Data not available

1. Mackerer, 1992.
2. AH: 1-5 ring [R] alkylated aromatic compounds (no heterocyclic compounds) as % total sample per procedure in Feuston et al., 1994.
3. Total material (Sulfur, N-PAC, S-PAC, Aromatics) as % total sample.
4. 3-7 ring PAC by DMSO extraction per procedure in Roy et al., 1988.
5. Samples 1-3: same crude, same refinery, three different viscosity ranges.
6. Range of 3-7 ring PACs by IP Method 346, Blackburn et al, 1996
7. Results and procedure presented in Fueston et al., 1994.
8. Samples 4-5: same crude, same refinery. Sample 6: different refinery.
9. Higher values of 3-7 ring PACs in RAE samples are reflective of contamination by, or intentional addition of vacuum distillate to residual oil prior to solvent extraction.